

Stability and electronic properties of carbon phosphide compounds with 1:1 stoichiometry

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The stability and electronic properties of various structures of carbon phosphide as well as other possible group IV-V compounds with 1:1 stoichiometry have been examined using first-principles calculations. Similar to CN, layered structures of CP are found to be energetically stable. Among all the structures considered in this study, the GaSe-like layered structure with fourfold coordination of group-IV atoms and threefold coordination of group-V atoms is energetically favorable for all group IV-V compounds except for the heaviest compound SnSb. The low-energy GaSe-like structure of CP has semiconductor characteristics, while other structures show metallic properties. With gradual change of group-IV element from C to Sn, and group-V element from N to Sb, sp^3 hybridization becomes energetically favorable.

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Due to the novel microstructures and extraordinary combination of physical and chemical properties¹ of carbon nitride, there has been a large amount of research worldwide on growing carbon nitride and related materials since the existence of β - C_3N_4 and its properties were predicted.^{2,3} β - C_3N_4 with expected hardness, as well as other CN_x phases with various C/N ratios have been successfully grown. The measured properties of β - C_3N_4 and α - C_3N_4 are in good agreement with predictions of *ab initio* calculations.¹

Recently, the synthesis of amorphous carbon phosphide films using radio frequency plasma deposition method has been reported by Pearce *et al.*⁴ The P/C ratios were found to be as high as 3:1 with $\sim 10\%$ H. Different P/C ratios can be achieved by controlling the ratio of PH_3/CH_4 in the gas mixture during the synthesis of carbon phosphide films.

The successful example of C_3N_4 demonstrated the power of first-principles methods in predicting properties of new materials. It would be useful to perform such calculations on carbon phosphide to understand its structural and electronic properties. In an earlier work,⁵ we have examined the stability of various structural forms of C_3P_4 using first-principles calculations⁶ based on the density functional theory (DFT).⁷ Our results showed that the pseudocubic phase (defect zinc blende structure) of C_3P_4 is more stable than many other possible structures such as α , β , cubic, and graphitic C_3P_4 .⁵ Our calculations also predicted that all the structures considered show anomalous metallic characteristics within the local density approximation (LDA).

In this work, we extend our investigation to carbon phosphide as well as other group IV-V compounds with a 1:1 stoichiometry. Several possible crystal structures were considered which included the eight structures suggested by Cote and Cohen for CN,⁸ i.e., rocksalt (NaCl), zinc blende (ZB), rhombohedral (rhomb.), bct4, H -6, GeP, β -InS, and GaSe. We also considered other structures such as the CsCl-like bcc structure and the β -tin structure. First principles calculations based on the DFT were performed to examine the stability and electronic properties of these structures.

The CASTEP code,^{6,9} with the ultrasoft pseudopotentials¹⁰ and the generalized gradient approximation (GGA-PW91)¹¹ for exchange and correlation, was used in our calculations. We used a cutoff energy of 310 eV in the plane wave expansion and special k points generated by Monkhorst-Pack scheme¹² for integration over the irreducible part of the Brillouin zone. Using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme,¹³ geometry optimization were performed under the preselected space group for the CsCl, NaCl, and zinc blende (ZB) structures while full structural relaxations (cell plus atomic positions) were carried out for other structures. The symmetry of the optimized structure in the latter case was then determined by examining the optimized structures with a 0.05 Å tolerance.

The total energies of CP in various structural forms are shown in Fig. 1 as functions of volume per atom. The structural details are also given in Table I. The CsCl structure and the GeP-like structure⁸ have much higher energies than the other structures and the results are not shown in the figure. However, the results of the CsCl structure are included in Table I for comparison. The high total energies of the CsCl- and GeP-like phases indicate that they are energetically unfavorable compared to other structures.

As in the case of carbon nitride,⁸ the rocksalt (NaCl) structure of CP is found to be mechanically unstable. It may transform to the β -tin structure or relax to the rhombohedral structure. Interestingly, the β -tin phase of CP is more stable than ZB phase in contrast to normal III-V and II-VI semiconductors. The low cohesive energies of CsCl, NaCl, and ZB phases of CP suggest that stable CP is not likely to adopt a cubic structural form. Rather, these high density cubic phases will transform into the tetragonal β -tin phase or the rhombohedral structure, with their density decreasing to 3.780 or 3.773 g/cm³ and their cohesive energy increasing to 4.977 or 4.980 eV/atom, respectively. The tetragonal β -tin and rhombohedral structures have very similar densities and cohesive energies. The difference between the cohesive energies of the two structures is only 0.003 eV/atom while the

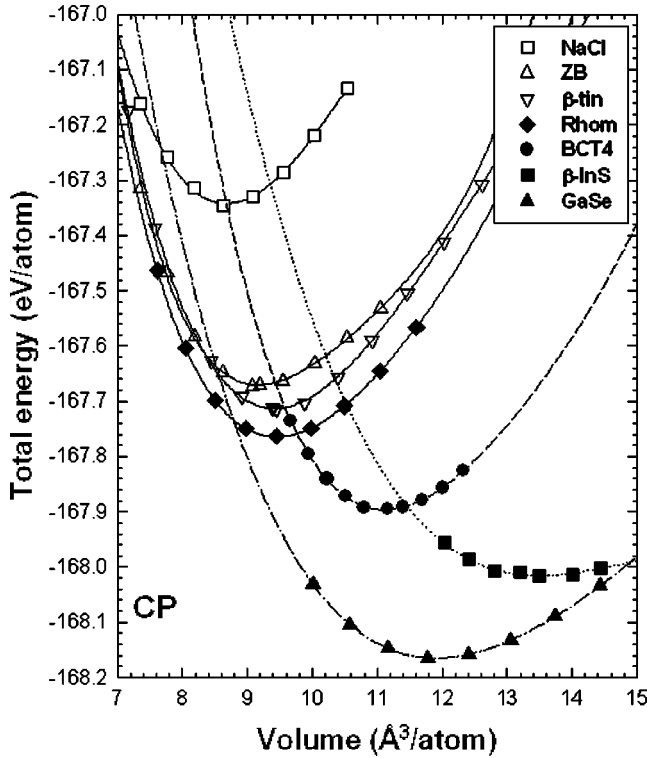


FIG. 1. Total energies (eV/atom) of various phases of CP are shown as a function of volume ($\text{\AA}^3/\text{atom}$).

difference in their densities is as small as 0.007 g/cm^3 . This indicates that mixed phases of tetragonal β -tin and rhombohedral structures are highly possible in synthesized CP films.

The H -6 (hexagonal structure with six atoms in a unit cell) and the bct4 (body-center tetragonal structure with four

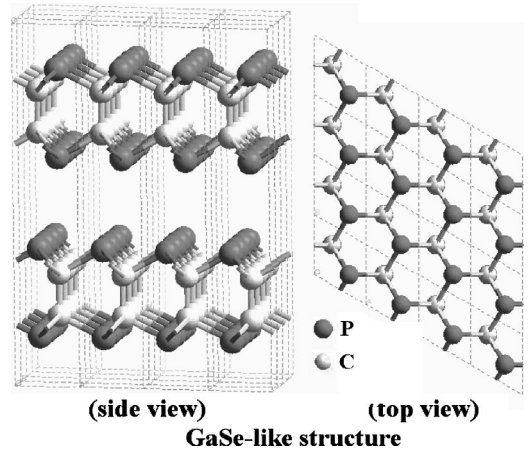


FIG. 2. Side and top views of CP compound in the GaSe structure which is predicted to be the most stable structure of CP. The positions of C (or P) atoms in the eight-atom hexagonal unit cell in terms of the lattice vectors are: $\pm(2/3, 1/3, w)$ and $\pm(1/3, 2/3, w+1/2)$ where $w(\text{C})=0.19226$ and $w(\text{P})=-0.37072$.

atoms per unit cell) structures are three dimensional (3D) structural forms with sp^2 bonding. Similar to CN, our calculations show that CP compounds in both structures have lower energy compared to the cubic phases such as the CsCl and the NaCl structures. Only the structural information of bct4 are given in Table I since its total energy is lower than that of the H -6 structure. The cohesive energy of CP in the bct4 structure is 5.114 eV/atom , which is larger than those of the ZB, β -tin, and rhombohedral structures.

We also considered two layered structures which are similar to the β -InS (orthorhombic) and GaSe (hexagonal) (Fig. 2) structures, respectively. It was found that these two struc-

TABLE I. The calculated structural properties [space group, density, lattice parameters, and bulk modulus (B)] and cohesive energy (E_{coh}) of carbon phosphide with 1:1 stoichiometry.

| Structure | Space group | Density (g/cm^3) | Lattice parameters (\AA) | B (GPa) | E_{coh} (eV/atom) |
|--------------|--------------------|--------------------------------|--|--------------|-------------------------------|
| CsCl | $Pm\bar{3}m$ (221) | 4.104 | $a=2.591$ | 170 | 3.465 |
| NaCl | $Fm\bar{3}m$ (225) | 4.135 | $a=4.102$ | 223 | 4.508 |
| ZB | $F\bar{4}3m$ (216) | 3.881 | $a=3.538$ | 182 | 4.890 |
| β -tin | $I\bar{4}m2$ (119) | 3.780 | $a=4.712$ $c=3.402$ | 205 | 4.977 |
| Rhom. | Cm (8) | 3.773 | $a=4.719$ $b=3.305$ $c=2.820$ $\beta=120.6^\circ$ | 183 | 4.980 |
| BCT4 | $I41md$ (109) | 3.198 | $a=2.925$ $c=10.434$ | 209 | 5.114 |
| β -InS | $Pbnm$ (62) | 2.644 | $a=4.987$ $b=7.618$ $c=2.842$ | 77 | 5.242 |
| GaSe | $P63/mmc$ (194) | 3.032 | $a=2.850$ $c=13.389$ $\gamma=120^\circ$ | 106 | 5.423 |

TABLE II. Bulk moduli of phosphides. (Experimental bulk moduli of AlP, GaP, and InP are from Ref. 17).

| Alloy | BP | CP (GaSe) | AlP | GaP | InP |
|-----------|---------------|-----------------|------|------|------|
| B (GPa) | 173 (Ref. 16) | 106 (this work) | 86.0 | 88.7 | 71.0 |

tures are energetically more stable than all other structures considered in this work. The cohesive energy of CP in the β -InS structure is 5.242 eV/atom and that of the GaSe structure is 5.423 eV/atom. Due to the layered arrangement of carbon and phosphorus, the densities of these two phases are low compared to the 3D structures. The density of CP in the GaSe structure is 3.032 g/cm³ while that of the β -InS structure 2.644 g/cm³, lowest among all the structural forms considered in our study.

Among the structures under consideration, CP in the NaCl structure has the largest bulk modulus (223 GPa), which is similar to the bulk modulus of SiC [224 GPa (Ref. 14)]. However, due to the high total energy (small cohesive energy) of the NaCl structure, CP is not likely to exist in the NaCl phase at ambient pressure. The bct4 and the rhombohedral structures have relatively high bulk moduli, i.e., 209 and 183 GPa, respectively. However, both of them are smaller than that of SiC, but comparable to that of AlN [206 GPa (Ref. 15)], and larger than that of BP [173 GPa (Ref. 16)]. As expected, the layered structures are soft. The β -InS structure is the softest phase with a bulk modulus of 77 GPa, while the GaSe structure, with a bulk modulus of 106 GPa, is only slightly harder than the β -InS structure. Compared with group III-P semiconductors, the most stable structural form of CP, i.e., the GaSe structure, is the second hardest, next to BP which has a bulk modulus of 173 GPa,¹⁶ as shown in Table II.

In our earlier work on C₃P₄,⁵ it was found that C₃P₄ in all the structures considered are metallic within LDA. In our present study of CP, we also found that all structural forms of CP exhibit metallic characteristics within GGA, except the GaSe-like structure which has significantly different electronic properties. The GaSe phase of CP shows semiconductor characteristics with direct band gap of 1.60 eV located at the K point in the Brillouin zone, as shown in Fig. 3. The real band gap of CP should be slightly larger since it is well known that GGA underestimates the band gap of semiconductors. The opening of the energy gap near the Fermi energy in turn enhances the stability of CP in the GaSe structure.

Analysis of bonding configuration is useful to understand structural stability. The GaSe structure of CP has unique bonding configuration compared to the other structures. Here the carbon atom has fourfold coordination while the phosphorous atom has threefold coordination. CP with the 1:1 stoichiometry has nine electrons per chemical formula which is one electron more than the eight electrons required to form the tetrahedral bonding as in a typical III-V or II-VI semiconductor. It is therefore not surprising that CP does not adopt the ZB or rocksalt (NaCl) structure. On the contrary, CP (and other IV-V type compounds) can be expected to be more stable in other unstoichiometric forms. This is demon-

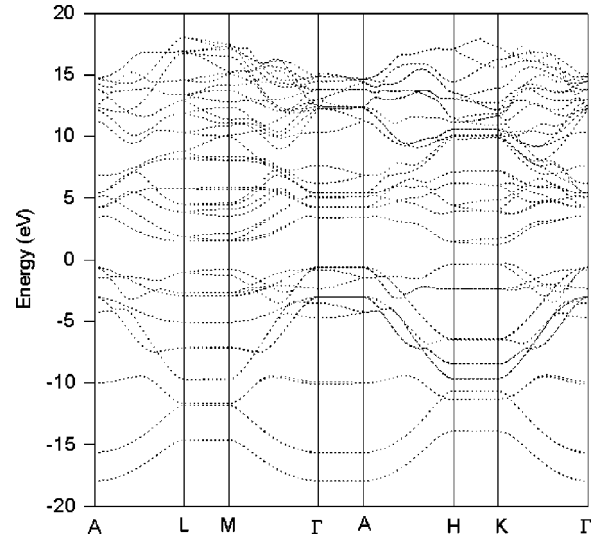


FIG. 3. The calculated band structure of CP in the GaSe structure (hexagonal). The Fermi energy is located at 0 eV.

strated by the fact that the low-energy structural phases of CP (the β -InS and the GaSe phases) are those of the III-VI compounds which also have nine valence electrons per formula unit. Further analysis of the bonding configuration of the optimized CP structure reveals that CP tends to be stabilized with fourfold bonding of C and threefold bonding of P, which is consistent with the number of valence electrons needed in C and P atoms to close the electronic shell. Interestingly, we also found that stable C₃P₄ in the pseudocubic phase have the same bonding characteristics, i.e., fourfold bonding of C and threefold bonding of P. The difference between the bonding configurations of CP in the GaSe phase and pseudocubic-C₃P₄ is that a carbon atom in CP (GaSe) forms three C-P bonds and one C-C bond with its neighbors while the carbon atom in pseudocubic-C₃P₄ is bonded to four phosphorous neighbors.

To further verify the bonding configuration and structural stability, we carried out a systematic investigation on the stability of other group IV-V (IV=C, Si, Ge, Sn and V=N, P, As, Sb) compounds. The results are given in Table III. For each compound, three typical structures were considered. The ZB structure represents sp^3 bonding and the bct4 is a typical structure with sp^2 bonding. The GaSe phase is also included because it is the most stable phase for most of the structures. In addition, the total energies of the three phases for each structure, we also presented the differences of the total energies of the bct4 phase and the GaSe phase relative to that of the ZB phase for each compound in Table III. The energy difference between the BCT4 phase and the ZB phase $\Delta E_{sp^2-sp^3} = E_{bct4} - E_{ZB}$, reveals the relative stability of these two phases and can be used as an indicator for preferred bonding configuration in a given compound. A positive $\Delta E_{sp^2-sp^3}$ means that the energy of the bct4 phase is higher than that of the ZB phase, and therefore, the ZB phase is more stable, which implies that sp^3 bonding is favored for the given compound, and vice versa. The results obtained for the various compounds considered show clearly that when the group-IV atom is gradually changed from C to Sn and the

TABLE III. Comparison of stability of structures with sp^3 hybridization (e.g., ZB structure) and sp^2 hybridization (e.g., bct4 structure) for C-V (V=N, P, As, Sb) and IV-P (IV=C, Si, Ge, Sn) compounds. The total energies of group IV-V compounds in GaSe structure are also shown for comparison. All energy values are given in eV/atom.

| Type | Alloy | Total energy | | E_{GaSe} | $\Delta E_{sp^2-sp^3}$ ($E_{\text{bct4}} - E_{\text{ZB}}$) | Bonding | $E_{\text{GaSe}} - E_{\text{ZB}}$ |
|------|-------|---------------------------------|-----------------------------------|-------------------|---|---------|-----------------------------------|
| | | E_{ZB} (3D sp^3) | E_{bct4} (3D sp^2) | | | | |
| C-V | CN | -211.8703 | -213.1402 | -213.8763 | -1.2699 | sp^2 | -2.0060 |
| | CP | -167.6712 | -167.8949 | -168.2045 | -0.2237 | sp^2 | -0.5333 |
| | CAs | -164.1814 | -164.2435 | -165.0164 | -0.0621 | sp^2 | -0.8350 |
| | CSb | -153.5312 | -153.3661 | -154.1676 | +0.1651 | sp^3 | -0.6364 |
| IV-P | CP | -167.6712 | -167.8949 | -168.2045 | -0.2237 | sp^2 | -0.5333 |
| | SiP | -144.5312 | -144.1273 | -144.9324 | +0.4039 | sp^3 | -0.4012 |
| | GeP | -144.9288 | -144.4934 | -145.1816 | +0.4354 | sp^3 | -0.2528 |
| | SnP | -139.4868 | -139.1079 | -139.6087 | +0.3789 | sp^3 | -0.1219 |

group-V atom changed from N to Sb, sp^3 hybridization becomes energetically favorable as compared to sp^2 hybridization.

We have also calculated the total energies of all the possible phases for each compound. It was found that all of these compounds, except SnSb, stabilize into the GaSe structure. However, as the group-IV atom is gradually changed from C to Sn and group-V atom changed from N to Sb, the stability of the GaSe phase become less prominent, as shown by the energy differences between the ZB phase and the GaSe phase given in Table III.

In summary, we have investigated the stabilities of CP and other group IV-V compounds with 1:1 stoichiometry, using

first-principles pseudopotential calculations. It is found that the GaSe-like layered structure with fourfold coordination of the group-IV atoms and threefold coordination of the group-V atoms are the most stable phase for CP and other group IV-V compounds with 1:1 stoichiometry, except for the heaviest compound SnSb. This low-energy GaSe-like structure of CP exhibits unique semiconductor characteristics with a direct band gap of 1.60 eV within GGA, which is in sharp contrast to the metallic behaviors we found for other structural forms of CP considered in this study and C_3P_4 in our previous work. Our first-principles computational results suggest various possibilities for designing carbon phosphides with interesting electronic properties in terms of composition and structural forms.

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